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(54) Title: MOLYBDENUM-BASED CATALYST COMPOSITION FOR POLYMERIZING CONJUGATED DIENES

(57) Abstract: A catalyst composition that is the combination of or the reaction product of ingredients including a molybdenum-containing compound, a hydrogen phosphite, and an organoaluminum compound. This catalyst composition is useful for polymerizing conjugated dienes and is particularly useful for polymerizing 1,3-butadiene into syndiotactic 1,2-polybutadiene.

MOLYBDENUM-BASED CATALYST COMPOSITION FOR POLYMERIZING CONJUGATED DIENES

FIELD OF THE INVENTION

5 The present invention generally relates to a catalyst composition for use in polymerizing conjugated dienes. More particularly, the present invention is directed toward a molybdenum-based catalyst composition that is formed by combining a molybdenum-containing compound, a hydrogen phosphite, and an organoaluminum compound. Advantageously, the molybdenum-based catalyst 10 composition of this invention can be used to polymerize 1,3-butadiene into 1,2-polybutadiene.

BACKGROUND OF THE INVENTION

15 Syndiotactic 1,2-polybutadiene is a crystalline thermoplastic resin that has a stereoregular structure in which the side chain vinyl groups are located alternately on the opposite sides in relation to the polymeric main chain. Syndiotactic 1,2-polybutadiene is a unique material that exhibits the properties of both plastics and rubber, and therefore it has many uses. For example, films, fibers, and molded articles can be made utilizing syndiotactic 1,2-polybutadiene. 20 It can also be blended into and co-cured with natural and synthetic rubbers.

25 Syndiotactic 1,2-polybutadiene can be made by solution, emulsion or suspension polymerization. Generally, syndiotactic 1,2-polybutadiene has a melting temperature within the range of about 195°C to about 215°C, but due to processability considerations, it is generally desirable for syndiotactic 1,2-polybutadiene to have a melting temperature of less than about 195°C.

30 Various transition metal catalyst systems based on cobalt, titanium, vanadium, and chromium for the preparation of syndiotactic 1,2-polybutadiene have been reported. The majority of these catalyst systems, however, have no practical utility because they have low catalytic activity or poor stereoselectivity, and in some cases they produce low molecular weight polymers or partially crosslinked polymers unsuitable for commercial use.

The following two cobalt-based catalyst systems are well known for the preparation of syndiotactic 1,2-polybutadiene on a commercial scale: (1) a catalyst system comprising cobalt bis(acetylacetone), triethylaluminum, water, and triphenylphosphine (U.S. Pat. Nos. 3,498,963 and 4,182,813), and (2) a catalyst system comprising cobalt tris(acetylacetone), triethylaluminum, and carbon disulfide (U.S. Pat. No. 3,778,424). These cobalt-based catalyst systems also have disadvantages.

The first cobalt catalyst system referenced above yields syndiotactic 1,2-polybutadiene having very low crystallinity. Also, this catalyst system develops sufficient catalytic activity only when halogenated hydrocarbon solvents are used as the polymerization medium, and halogenated solvents present toxicity problems.

The second cobalt catalyst system referenced above uses carbon disulfide as one of the catalyst components. Because of its low flash point, obnoxious smell, high volatility, and toxicity, carbon disulfide is difficult and dangerous to use, and requires expensive safety measures to prevent even minimal amounts escaping into the atmosphere. Furthermore, the syndiotactic 1,2-polybutadiene produced with this cobalt catalyst system has a very high melting temperature of about 200-210 °C, which makes it difficult to process the polymer. Although the melting temperature of the syndiotactic 1,2-polybutadiene produced with this cobalt catalyst system can be reduced by employing a catalyst modifier as a fourth catalyst component, the presence of this catalyst modifier has adverse effects on the catalyst activity and polymer yields. Accordingly, many restrictions are required for the industrial utilization of these cobalt-based catalyst systems.

Coordination catalyst systems based on molybdenum-containing compounds, such as the combination of molybdenum acetylacetone and triethylaluminum, have been known for some time, but they have shown very low catalytic activity and poor stereoselectivity for the polymerization of conjugated dienes. The product mixture often contains oligomers, low molecular weight liquid polymers, or partially crosslinked polymers. Therefore, these molybdenum-based catalyst systems have no industrial utility.

U.S. Pat. No. 3,336,280 discloses a process for polymerizing 1,3-butadiene to rubbery 1,2-polybutadiene by using a catalyst system comprising

molybdenum pentachloride, a trialkylaluminum compound, and a promoter compound selected from ethers, amines, amides, and alkylideneamines. U.S. Pat. No. 3,451,987 describes a process for preparing amorphous 1,2-polybutadiene by polymerizing 1,3-butadiene in the presence of a catalyst system comprising a 5 molybdenum halide or oxyhalide and a dialkylaluminum alkoxide. Japanese Pat. No. 75,154,389 (see *Chemical Abstracts* 1976, Vol. 84, 151913k) discloses a process that produces rubbery 1,2-polybutadiene by polymerizing 1,3-butadiene in the presence of a catalyst system consisting of molybdenum pentachloride, an 10 organoaluminum compound, and phenol. U.S. Pat. No. 4,912,182 discloses a process for synthesizing high-vinyl polybutadiene by polymerizing 1,3-butadiene in the presence of a catalyst system comprising a molybdenum-containing compound prepared by modifying molybdenum pentachloride, molybdenum 15 trichloride, or molybdenum tetrachloride with an alkyl carboxylic acid or an aryl carboxylic acid, and an aluminum-containing compound prepared by modifying a trialkylaluminum compound with 2-allylphenol. These molybdenum catalyst systems, however, produce amorphous atactic 1,2-polybutadiene, which has no 20 crystallinity.

Because syndiotactic 1,2-polybutadiene is useful and the catalysts known heretofore in the art have many shortcomings, it would be advantageous to develop 25 a new and significantly improved catalyst composition that has high catalytic activity and stereoselectivity for polymerizing 1,3-butadiene into 1,2-polybutadiene.

SUMMARY OF THE INVENTION

25 In general, the present invention provides a catalyst composition that is the combination of or the reaction product of ingredients comprising a molybdenum-containing compound, a hydrogen phosphite, and an organoaluminum compound.

The present invention also provides a catalyst composition formed by a 30 process comprising the step of combining a molybdenum-containing compound, a hydrogen phosphite, and an organoaluminum compound.

The present invention also provides a process for preparing conjugated diene polymers, the process comprising the step of polymerizing conjugated diene monomers in the presence of a catalytically effective amount of a catalyst composition formed by combining a molybdenum-containing compound, a 5 hydrogen phosphite, and an organoaluminum compound.

The present invention further provides a process for preparing syndiotactic 1,2-polybutadiene, the process comprising the step of polymerizing 1,3-butadiene in the presence of a catalytically effective amount of a catalyst composition formed by combining a molybdenum-containing compound, a 10 hydrogen phosphite, and an organoaluminum compound.

The present invention also provides a conjugated diene polymer that is prepared by polymerizing conjugated diene monomers with a catalyst composition formed by a process comprising the step of combining a molybdenum-containing compound, a hydrogen phosphite, and an organoaluminum compound.

The present invention also provides a syndiotactic 1,2-polybutadiene polymer that is prepared by polymerizing 1,3-butadiene monomer with a catalyst composition formed by a process comprising the step of combining a molybdenum-containing compound, a hydrogen phosphite, and an organoaluminum compound.

Advantageously, the catalyst composition of the present invention has 20 very high catalytic activity and selectivity for polymerizing conjugated diene monomers such as 1,3-butadiene. This activity and selectivity, among other advantages, allows syndiotactic 1,2-polybutadiene to be produced in very high yields with low catalyst levels after relatively short polymerization times. Significantly, the catalyst composition of this invention is very versatile and capable 25 of producing syndiotactic 1,2-polybutadiene with a wide range of melting temperatures without the need for a catalyst modifier that may have adverse affects on the catalyst activity and polymer yields. In addition, the catalyst composition of this invention does not contain carbon disulfide, which is highly volatile, toxic, and flammable, and therefore the toxicity, objectionable smell, dangers, and 30 expense associated with the use of carbon disulfide is eliminated. Moreover, this catalyst composition is molybdenum-based, and molybdenum compounds are generally stable, inexpensive, relatively innocuous, and readily available.

Additionally, this catalyst composition has high catalytic activity in a wide variety of solvents including the environmentally-preferred nonhalogenated solvents, such as aliphatic and cycloaliphatic hydrocarbons.

5

DETAILED DESCRIPTION OF ILLUSTRATIVE EMBODIMENTS

10 The present invention is generally directed toward a molybdenum-based catalyst composition, methods of using this catalyst composition for polymerizing conjugated dienes, and the resulting polymers. It has now been found that conjugated dienes can be efficiently polymerized with a molybdenum-based catalyst composition. In particular, 1,3-butadiene can be efficiently polymerized into syndiotactic 1,2-polybutadiene by using this catalyst composition.

15 The catalyst composition of the present invention is formed by combining (a) a molybdenum-containing compound, (b) a hydrogen phosphite, and (c) an organoaluminum compound. In addition to the three catalyst ingredients (a), (b), and (c), other organometallic compounds or Lewis bases can also be added, if desired.

20 Various molybdenum-containing compounds or mixtures thereof can be employed as ingredient (a) of the catalyst composition of this invention. It is generally advantageous to employ molybdenum-containing compounds that are soluble in hydrocarbon solvents such as aromatic hydrocarbons, aliphatic hydrocarbons, or cycloaliphatic hydrocarbons. Hydrocarbon-insoluble molybdenum-containing compounds, however, can be suspended in the polymerization medium to form the catalytically active species and are therefore also useful.

25

The molybdenum atom in the molybdenum-containing compounds can be in various oxidation states ranging from 0 up to +6. Suitable types of molybdenum-containing compounds that can be utilized include, but are not limited to, molybdenum carboxylates, molybdenum organophosphates, molybdenum organophosphonates, molybdenum organophosphinates, molybdenum carbamates, molybdenum dithiocarbamates, molybdenum xanthates, molybdenum β -diketonates, molybdenum alkoxides or aryloxides, molybdenum

halides, molybdenum pseudo-halides, molybdenum oxyhalides, and organomolybdenum compounds.

Some specific examples of suitable molybdenum carboxylates include molybdenum formate, molybdenum acetate, molybdenum acrylate, molybdenum 5 methacrylate, molybdenum valerate, molybdenum gluconate, molybdenum citrate, molybdenum fumarate, molybdenum lactate, molybdenum maleate, molybdenum oxalate, molybdenum 2-ethylhexanoate, molybdenum neodecanoate, molybdenum naphthenate, molybdenum stearate, molybdenum oleate, molybdenum benzoate, and molybdenum picolinate.

10 Some specific examples of suitable molybdenum organophosphates include molybdenum dibutyl phosphate, molybdenum dipentyl phosphate, molybdenum dihexyl phosphate, molybdenum diheptyl phosphate, molybdenum dioctyl phosphate, molybdenum bis(1-methylheptyl) phosphate, molybdenum bis(2-ethylhexyl) phosphate, molybdenum didecyl phosphate, molybdenum 15 didodecyl phosphate, molybdenum dioctadecyl phosphate, molybdenum dioleyl phosphate, molybdenum diphenyl phosphate, molybdenum bis(p-nonylphenyl) phosphate, molybdenum butyl (2-ethylhexyl) phosphate, molybdenum (1-methylheptyl) (2-ethylhexyl) phosphate, and molybdenum (2-ethylhexyl) (p-nonylphenyl) phosphate.

20 Some specific examples of suitable molybdenum organophosphonates include molybdenum butyl phosphonate, molybdenum pentyl phosphonate, molybdenum hexyl phosphonate, molybdenum heptyl phosphonate, molybdenum octyl phosphonate, molybdenum (1-methylheptyl) phosphonate, molybdenum (2-ethylhexyl) phosphonate, molybdenum decyl phosphonate, molybdenum 25 dodecyl phosphonate, molybdenum octadecyl phosphonate, molybdenum oleyl phosphonate, molybdenum phenyl phosphonate, molybdenum (p-nonylphenyl) phosphonate, molybdenum butyl butylphosphonate, molybdenum pentyl pentylphosphonate, molybdenum hexyl hexylphosphonate, molybdenum heptyl heptylphosphonate, molybdenum octyl octylphosphonate, molybdenum 30 (1-methylheptyl) (1-methylheptyl)phosphonate, molybdenum (2-ethylhexyl) (2-ethylhexyl)phosphonate, molybdenum decyl decylphosphonate, molybdenum dodecyl dodecylphosphonate, molybdenum octadecyl octadecylphosphonate,

5 molybdenum oleyl oleylphosphonate, molybdenum phenyl phenylphosphonate, molybdenum (p-nonylphenyl) (p-nonylphenyl)phosphonate, molybdenum butyl (2-ethylhexyl)phosphonate, molybdenum (2-ethylhexyl) butylphosphonate, molybdenum (1-methylheptyl) (2-ethylhexyl)phosphonate, molybdenum (2-
10 ethylhexyl) (1-methylheptyl)phosphonate, molybdenum (2-ethylhexyl) (p-nonylphenyl)phosphonate, and molybdenum (p-nonylphenyl) (2-ethylhexyl)phosphonate.

Some specific examples of suitable molybdenum organophosphinates include molybdenum butylphosphinate, molybdenum pentylphosphinate, molybdenum hexylphosphinate, molybdenum heptylphosphinate, molybdenum octylphosphinate, molybdenum (1-methylheptyl)phosphinate, molybdenum (2-ethylhexyl)phosphinate, molybdenum decylphosphinate, molybdenum dodecylphosphinate, molybdenum octadecylphosphinate, molybdenum oleylphosphinate, molybdenum phenylphosphinate, molybdenum (p-nonylphenyl)phosphinate, molybdenum dibutylphosphinate, molybdenum dipentylphosphinate, molybdenum dihexylphosphinate, molybdenum diheptylphosphinate, molybdenum dioctylphosphinate, molybdenum bis(1-methylheptyl)phosphinate, molybdenum bis(2-ethylhexyl)phosphinate, molybdenum didecylphosphinate, molybdenum didodecylphosphinate, molybdenum dioctadecylphosphinate, molybdenum dioleylphosphinate, molybdenum diphenylphosphinate, molybdenum bis(p-nonylphenyl)phosphinate, molybdenum butyl(2-ethylhexyl)phosphinate, molybdenum (1-methylheptyl)(2-ethylhexyl)phosphinate, and molybdenum (2-ethylhexyl)(p-nonylphenyl)phosphinate.

25 Some specific examples of suitable molybdenum carbamates include molybdenum dimethylcarbamate, molybdenum diethylcarbamate, molybdenum diisopropylcarbamate, molybdenum dibutylcarbamate, and molybdenum dibenzylcarbamate.

30 Some specific examples of suitable molybdenum dithiocarbamates include molybdenum dimethyldithiocarbamate, molybdenum diethyldithiocarbamate, molybdenum diisopropylidithiocarbamate, molybdenum dibutyldithiocarbamate, and molybdenum dibenzylidithiocarbamate.

Some specific examples of suitable molybdenum xanthates include molybdenum methylxanthate, molybdenum ethylxanthate, molybdenum isopropylxanthate, molybdenum butylxanthate, and molybdenum benzylxanthate.

Some specific examples of suitable molybdenum β -diketonates include
5 molybdenum acetylacetone, molybdenum trifluoroacetylacetone, molybdenum hexafluoroacetylacetone, molybdenum benzoylacetone, molybdenum 2,2,6,6-tetramethyl-3,5-heptanedionate, molybdenum dioxide bis(acetylacetone), molybdenum dioxide bis(trifluoroacetylacetone),
10 molybdenum dioxide bis(hexafluoroacetylacetone), molybdenum dioxide bis(benzoylacetone), and molybdenum dioxide bis(2,2,6,6-tetramethyl-3,5-heptanedionate).

Some specific examples of suitable molybdenum alkoxides or aryloxides include molybdenum methoxide, molybdenum ethoxide, molybdenum isopropoxide, molybdenum 2-ethylhexoxide, molybdenum phenoxide, molybdenum 15 nonylphenoxide, and molybdenum naphthoxide.

Some specific examples of suitable molybdenum halides include molybdenum hexafluoride, molybdenum pentafluoride, molybdenum tetrafluoride, molybdenum trifluoride, molybdenum pentachloride, molybdenum tetrachloride, molybdenum trichloride, molybdenum tetrabromide, molybdenum tribromide, 20 molybdenum triiodide, and molybdenum diiodide.

Some specific examples of suitable molybdenum pseudo-halides include molybdenum cyanide, molybdenum cyanate, molybdenum thiocyanate, and molybdenum azide.

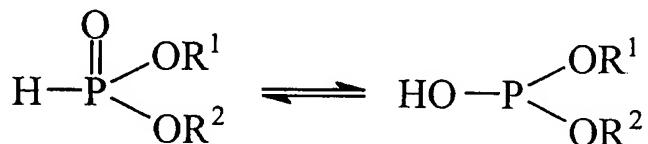
Some specific examples of suitable molybdenum oxyhalides include
25 molybdenum oxytetrafluoride, molybdenum dioxydifluoride, molybdenum oxytetrachloride, molybdenum oxytrichloride, molybdenum dioxydichloride, molybdenum oxytribromide, and molybdenum dioxydibromide.

The term "organomolybdenum compound" refers to any molybdenum compound containing at least one molybdenum-carbon bond. Some specific 30 examples of suitable organomolybdenum compounds include tris(allyl)molybdenum, tris(methallyl)molybdenum, tris(crotyl)molybdenum, bis(cyclopentadienyl)molybdenum, bis(ethylbenzene)molybdenum,

bis(pentamethylcyclopentadienyl)molybdenum, bis(mesitylene)molybdenum, bis(pentadienyl)molybdenum, bis(2,4-dimethylpentadienyl)molybdenum, bis(allyl)tricarbonylmolybdenum, (cyclopentadienyl)(pentadienyl)molybdenum, tetra(1-norbornyl)molybdenum (trimethylenemethane)tetracarbonylmolybdenum, 5 bis(butadiene)dicarbonylmolybdenum, (butadiene)tetracarbonylmolybdenum, and bis(cyclooctatetraene)molybdenum.

Useful hydrogen phosphite compounds that can be employed as ingredient (b) of the catalyst composition of this invention are acyclic hydrogen phosphites, cyclic hydrogen phosphites, and mixtures thereof.

10 In general, acyclic hydrogen phosphites may be represented by the following keto-enol tautomeric structures:



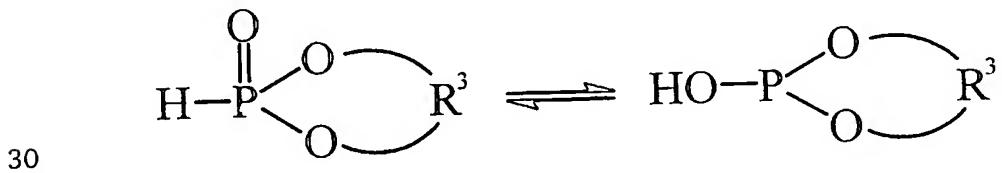
15

where R¹ and R², which may be the same or different, are mono-valent organic groups. Preferably, R¹ and R² are hydrocarbyl groups such as, but not limited to, alkyl, cycloalkyl, substituted cycloalkyl, alkenyl, cycloalkenyl, substituted cycloalkenyl, aryl, allyl, substituted aryl, aralkyl, alkaryl, and alkynyl groups, with each group preferably containing from 1 carbon atom, or the appropriate minimum number of carbon atoms to form the group, up to 20 carbon atoms. These hydrocarbyl groups may contain heteroatoms such as, but not limited to, nitrogen, oxygen, silicon, sulfur, and phosphorus atoms. The acyclic hydrogen phosphites exist mainly as the keto tautomer (shown on the left), with the enol tautomer (shown on the right) being the minor species. The equilibrium constant for the above-mentioned tautomeric equilibrium is dependent upon factors such as the temperature, the types of R¹ and R² groups, the type of solvent, and the like. Both 20 25

tautomers may be associated in dimeric, trimeric or oligomeric forms by hydrogen bonding. Either of the two tautomers or mixtures thereof can be employed.

Some representative and non-limiting examples of suitable acyclic hydrogen phosphites are dimethyl hydrogen phosphite, diethyl hydrogen phosphite, dibutyl hydrogen phosphite, dihexyl hydrogen phosphite, dioctyl hydrogen phosphite, didecyl hydrogen phosphite, didodecyl hydrogen phosphite, dioctadecyl hydrogen phosphite, bis(2,2,2-trifluoroethyl) hydrogen phosphite, diisopropyl hydrogen phosphite, bis(3,3-dimethyl-2-butyl) hydrogen phosphite, bis(2,4-dimethyl-3-pentyl) hydrogen phosphite, di-t-butyl hydrogen phosphite, bis(2-ethylhexyl) hydrogen phosphite, di-neopentyl hydrogen phosphite, bis(cyclopropylmethyl) hydrogen phosphite, bis(cyclobutylmethyl) hydrogen phosphite, bis(cyclopentylmethyl) hydrogen phosphite, bis(cyclohexylmethyl) hydrogen phosphite, dicyclobutyl hydrogen phosphite, dicyclopentyl hydrogen phosphite, dicyclohexyl hydrogen phosphite, dimethyl hydrogen phosphite, diphenyl hydrogen phosphite, dinaphthyl hydrogen phosphite, dibenzyl hydrogen phosphite, bis(1-naphthylmethyl) hydrogen phosphite, diallyl hydrogen phosphite, dimethallyl hydrogen phosphite, dicrotyl hydrogen phosphite, ethyl butyl hydrogen phosphite, methyl hexyl hydrogen phosphite, methyl neopentyl hydrogen phosphite, methyl phenyl hydrogen phosphite, methyl cyclohexyl hydrogen phosphite, methyl benzyl hydrogen phosphite, and the like. Mixtures of the above dihydrocarbyl hydrogen phosphites may also be utilized.

In general, cyclic hydrogen phosphites contain a divalent organic group that bridges between the two oxygen atoms that are singly-bonded to the phosphorus atom. These cyclic hydrogen phosphites may be represented by the following keto-enol tautomeric structures:



where R^3 is a divalent organic group. Preferably, R^3 is a hydrocarbylene group such as, but not limited to, alkylene, cycloalkylene, substituted alkylene, substituted cycloalkylene, alkenylene, cycloalkenylene, substituted alkenylene, substituted cycloalkenylene, arylene, and substituted arylene groups, with each 5 group preferably containing from 1 carbon atom, or the appropriate minimum number of carbon atoms to form the group, up to 20 carbon atoms. These hydrocarbylene groups may contain heteroatoms such as, but not limited to, nitrogen, oxygen, silicon, sulfur, and phosphorus atoms. The cyclic hydrogen phosphites exist mainly as the keto tautomer (shown on the left), with the enol 10 tautomer (shown on the right) being the minor species. The equilibrium constant for the above-mentioned tautomeric equilibrium is dependent upon factors such as the temperature, the types of R^3 group, the type of solvent, and the like. Both tautomers may be associated in dimeric, trimeric or oligomeric forms by hydrogen bonding. Either of the two tautomers or mixtures thereof can be used.

15 The cyclic hydrogen phosphites may be synthesized by the transesterification reaction of an acyclic dihydrocarbyl hydrogen phosphite (usually dimethyl hydrogen phosphite or diethyl hydrogen phosphite) with an alkylene diol or an arylene diol. Procedures for this transesterification reaction are well known to those skilled in the art. Typically, the transesterification reaction is carried out 20 by heating a mixture of an acyclic dihydrocarbyl hydrogen phosphite and an alkylene diol or an arylene diol. Subsequent distillation of the side-product alcohol (usually methanol or ethanol) that results from the transesterification reaction leaves the new-made cyclic hydrogen phosphite.

25 Some specific examples of suitable cyclic alkylene hydrogen phosphites are 2-oxo-(2H)-5-butyl-5-ethyl-1,3,2-dioxaphosphorinane, 2-oxo-(2H)-5,5-dimethyl-1,3,2-dioxaphosphorinane, 2-oxo-(2H)-1,3,2-dioxaphosphorinane, 2-oxo-(2H)-4-methyl-1,3,2-dioxaphosphorinane, 2-oxo-(2H)-5-ethyl-5-methyl-1,3,2-dioxaphosphorinane, 2-oxo-(2H)-5,5-diethyl-1,3,2-dioxaphosphorinane, 2-oxo-(2H)-5-methyl-5-propyl-1,3,2-dioxaphosphorinane, 2-oxo-(2H)-4-isopropyl-5,5-dimethyl-1,3,2-dioxaphosphorinane, 2-oxo-(2H)-4,6-dimethyl-1,3,2-dioxaphosphorinane, 2-oxo-(2H)-4-propyl-5-ethyl-1,3,2-dioxaphosphorinane, 2-oxo-(2H)-4-methyl-1,3,2-dioxaphospholane, 2-oxo-(2H)-4,5-dimethyl-1,3,2-

dioxaphospholane, 2-oxo-(2H)-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane, and the like. Mixtures of the above cyclic alkylene hydrogen phosphites may also be utilized.

Some specific examples of suitable cyclic arylene hydrogen phosphites 5 are 2-oxo-(2H)-4,5-benzo-1,3,2-dioxaphospholane, 2-oxo-(2H)-4,5-(3-methylbenzo)-1,3,2-dioxaphospholane, 2-oxo-(2H)-4,5-(4-methylbenzo)-1,3,2-dioxaphospholane, 2-oxo-(2H)-4,5-(4-tert-butylbenzo)-1,3,2-dioxaphospholane, 2-oxo-(2H)-4,5-naphthalo-1,3,2-dioxaphospholane, and the like. Mixtures of the above cyclic arylene hydrogen phosphites may also be utilized.

10 The molybdenum-based catalyst composition of this invention further comprises an organoaluminum compound, which has been designated as ingredient (c). As used herein, the term "organoaluminum compound" refers to any aluminum compound containing at least one aluminum-carbon bond. It is generally advantageous to employ organoaluminum compounds that are soluble 15 in a hydrocarbon solvent.

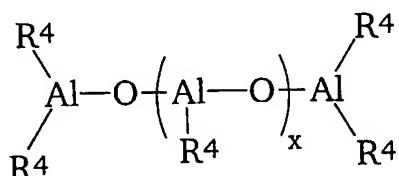
A preferred class of organoaluminum compounds that can be utilized is represented by the general formula AlR_nX_{3-n} , where each R, which may be the same or different, is a mono-valent organic group that is attached to the aluminum atom via a carbon atom, where each X, which may be the same or different, is a 20 hydrogen atom, a halogen atom, a carboxylate group, an alkoxide group, or an aryloxide group, and where n is an integer of 1 to 3. Preferably, each R is a hydrocarbyl group such as, but not limited to, alkyl, cycloalkyl, substituted cycloalkyl, alkenyl, cycloalkenyl, substituted cycloalkenyl, aryl, allyl, substituted aryl, aralkyl, alkaryl, and alkynyl groups, with each group preferably containing 25 from 1 carbon atom, or the appropriate minimum number of carbon atoms to form the group, up to about 20 carbon atoms. These hydrocarbyl groups may contain heteroatoms such as, but not limited to, nitrogen, oxygen, silicon, sulfur, and phosphorus atoms. Preferably, each X is a carboxylate group, an alkoxide group, or an aryloxide group, with each group preferably containing from 1 carbon atom, 30 or the appropriate minimum number of carbon atoms to form the group, up to about 20 carbon atoms.

Thus, some suitable types of organoaluminum compounds that can be utilized include, but are not limited to, trihydrocarbylaluminum, dihydrocarbylaluminum hydride, hydrocarbylaluminum dihydride, hydrocarbylaluminum dihalide, dihydrocarbylaluminum halide, dihydrocarbylaluminum carboxylate, hydrocarbylaluminum bis(carboxylate), dihydrocarbylaluminum alkoxide, hydrocarbylaluminum dialkoxide, dihydrocarbylaluminum aryloxide, hydrocarbylaluminum diaryloxide, and the like, and mixtures thereof. Trihydrocarbylaluminum compounds are generally preferred.

Some specific examples of organoaluminum compounds that can be utilized include trimethylaluminum, triethylaluminum, triisobutylaluminum, tri-n-propylaluminum, triisopropylaluminum, tri-n-butylaluminum, tri-n-hexylaluminum, tri-n-octylaluminum, tricyclohexylaluminum, triphenylaluminum, tri-p-tolyl-aluminum, tribenzylaluminum, diethylphenylaluminum, diethyl-p-tolylaluminum, diethylbenzylaluminum, ethyldiphenylaluminum, ethyldi-p-tolylaluminum, ethyl-dibenzylaluminum, diethylaluminum hydride, di-n-propylaluminum hydride, diisopropylaluminum hydride, di-n-butylaluminum hydride, diisobutylaluminum hydride, di-n-octylaluminum hydride, diphenylaluminum hydride, di-p-tolyl-aluminum hydride, dibenzylaluminum hydride, phenylethylaluminum hydride, phenyl-n-propylaluminum hydride, phenylisopropylaluminum hydride, phenyl-n-butylaluminum hydride, phenylisobutylaluminum hydride, phenyl-n-octylaluminum hydride, p-tolylethylaluminum hydride, p-tolyl-n-propylaluminum hydride, p-tolylisopropylaluminum hydride, p-tolyl-n-butylaluminum hydride, p-tolylisobutylaluminum hydride, p-tolyl-n-octylaluminum hydride, benzylethylaluminum hydride, benzyl-n-propylaluminum hydride, benzylisopropylaluminum hydride, benzyl-n-butylaluminum hydride, benzylisobutylaluminum hydride, and benzyl-n-octylaluminum hydride, ethylaluminum dihydride, n-propylaluminum dihydride, isopropylaluminum dihydride, n-butylaluminum dihydride, isobutylaluminum dihydride, n-octylaluminum dihydride, dimethylaluminum chloride, diethylaluminum chloride, diisobutylaluminum chloride, dimethylaluminum bromide, diethylaluminum bromide, dimethylaluminum fluoride, diethylaluminum

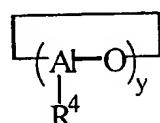
fluoride, methylaluminum dichloride, ethylaluminum dichloride, isobutylaluminum dichloride, methylaluminum dibromide, ethylaluminum dibromide, methylaluminum difluoride, ethylaluminum difluoride, methylaluminum sesquichloride, ethylaluminum sesquichloride, isobutylaluminum sesquichloride, 5 dimethylaluminum hexanoate, diethylaluminum octoate, diisobutylaluminum 2-ethylhexanoate, dimethylaluminum neodecanoate, diethyl-aluminum stearate, diisobutylaluminum oleate, methylaluminum bis(hexanoate), ethylaluminum bis(octoate), isobutylaluminum bis(2-ethylhexanoate), methyl-aluminum bis(neodecanoate), ethylaluminum bis(stearate), isobutylaluminum bis(oleate), 10 dimethylaluminum methoxide, diethylaluminum methoxide, diisobutyl-aluminum methoxide, dimethylaluminum ethoxide, diethylaluminum ethoxide, diisobutylaluminum ethoxide, dimethylaluminum phenoxide, diethylaluminum phenoxide, diisobutylaluminum phenoxide, methylaluminum dimethoxide, ethylaluminum dimethoxide, isobutylaluminum dimethoxide, methylaluminum diethoxide, ethylaluminum diethoxide, isobutylaluminum diethoxide, methyl- 15 aluminum diphenoxide, ethylaluminum diphenoxide, isobutylaluminum diphenoxide, and the like, and mixtures thereof.

Another class of organoaluminum compounds that can be utilized is aluminoxanes. Aluminoxanes are well known in the art and comprise oligomeric linear aluminoxanes that can be represented by the general formula:



25

and oligomeric cyclic aluminoxanes that can be represented by the general formula:



30

where x is an integer of 1 to about 100, preferably about 10 to about 50; y is an integer of 2 to about 100, preferably about 3 to about 20; and each R⁴, which may be the same or different, is a mono-valent organic group that is attached to the aluminum atom via a carbon atom. Preferably, each R⁴ is a hydrocarbyl group such as, but not limited to, alkyl, cycloalkyl, substituted cycloalkyl, alkenyl, cycloalkenyl, substituted cycloalkenyl, aryl, allyl, substituted aryl, aralkyl, alkaryl, and alkynyl groups, with each group preferably containing from 1 carbon atoms, or the appropriate minimum number of carbon atoms to form the group, up to about 20 carbon atoms. These hydrocarbyl groups may contain heteroatoms such as, but not limited to, nitrogen, oxygen, silicon, sulfur, and phosphorus atoms. It should be noted that the number of moles of the aluminoxane as used in this application refers to the number of moles of the aluminum atoms rather than the number of moles of the oligomeric aluminoxane molecules. This convention is commonly employed in the art of catalysis utilizing aluminoxanes.

In general, aluminoxanes can be prepared by reacting trihydrocarbylaluminum compounds with water. This reaction can be performed according to known methods, such as (1) a method in which the trihydrocarbylaluminum compound is dissolved in an organic solvent and then contacted with water, (2) a method in which the trihydrocarbylaluminum compound is reacted with water of crystallization contained in, for example, metal salts, or water adsorbed in inorganic or organic compounds, and (3) a method in which the trihydrocarbylaluminum compound is added to the monomer or monomer solution that is to be oligomerized, and then water is added.

Some specific examples of aluminoxane compounds that can be utilized include methylaluminoxane (MAO), modified methylaluminoxane (MMAO), ethylaluminoxane, butylaluminoxane, isobutylaluminoxane, and the like, and mixtures thereof. Isobutylaluminoxane is particularly useful on the grounds of its availability and its solubility in aliphatic and cycloaliphatic hydrocarbon solvents. Modified methylaluminoxane can be formed by substituting about 20-80% of the methyl groups of methylaluminoxane with C₂ to C₁₂ hydrocarbyl groups, preferably with isobutyl groups, by using techniques known to those skilled in the art.

The catalyst composition of this invention has very high catalytic activity over a wide range of catalyst concentrations and catalyst ingredient ratios. The polymers having the most desirable properties, however, are obtained within a narrower range of catalyst concentrations and catalyst ingredient ratios. Further, 5 it is believed that the three catalyst ingredients (a), (b), and (c) can interact to form an active catalyst species. Accordingly, the optimum concentration for any one catalyst ingredient is dependent upon the concentrations of the other catalyst ingredients. The molar ratio of the hydrogen phosphite to the molybdenum-containing compound (P/Mo) can be varied from about 0.5:1 to 10 about 50:1, more preferably from about 1:1 to about 25:1, and even more preferably from about 2:1 to about 10:1. Where ingredient (c) of the catalyst composition of the present invention comprises organoaluminum compounds defined by the formula AlR_nX_{3-n} , the molar ratio of the organoaluminum compound to the molybdenum-containing compound (Al/Mo) can be varied from 15 about 1:1 to about 100:1, more preferably from about 3:1 to about 50:1, and even more preferably from about 5:1 to about 25:1. When ingredient (c) of the catalyst composition of the present invention comprises an aluminoxane, the molar ratio of the aluminoxane to the molybdenum-containing compound (Al/Mo) can be varied from about 5:1 to about 500:1, more preferably from about 10:1 to about 20 200:1, and even more preferably from about 20:1 to about 100:1.

As discussed above, the catalyst composition of the present invention is preferably formed by combining the three catalyst ingredients (a), (b), and (c). Although an active catalyst species is believed to result from this combination, the degree of interaction or reaction between the various ingredients or components 25 is not known with any great degree of certainty. Therefore, it should be understood that the term "catalyst composition" has been employed to encompass a simple mixture of the ingredients, a complex of the various ingredients that is caused by physical or chemical forces of attraction, a chemical reaction product of the ingredients, or a combination of the foregoing.

30 The catalyst composition of the present invention can be formed by combining or mixing the catalyst ingredients or components by using, for example, one of the following methods:

First, the catalyst composition may be formed *in situ* by adding the three catalyst ingredients to a solution containing monomer and solvent, or simply bulk monomer, in either a stepwise or simultaneous manner. When adding the catalyst ingredients in a stepwise manner, the sequence in which the ingredients are added is not critical. Preferably, however, the molybdenum-containing compound is added first, followed by the hydrogen phosphite, and then followed by the organoaluminum compound.

Second, the three catalyst ingredients may be pre-mixed outside the polymerization system at an appropriate temperature, which is generally from about -20°C to about 80 °C, and the resulting catalyst composition is then added to the monomer solution.

Third, the catalyst composition may be pre-formed in the presence of monomer. That is, the three catalyst ingredients are pre-mixed in the presence of a small amount of monomer at an appropriate temperature, which is generally from about -20°C to about 80 °C. The amount of monomer that is used for the catalyst pre-forming can range from about 1 to about 500 moles per mole of the molybdenum-containing compound, more preferably from about 4 to about 100 moles per mole of the molybdenum-containing compound, and even more preferably from about 10 to about 50 moles per mole of the molybdenum-containing compound. The resulting catalyst composition is then added to the remainder of the monomer that is to be polymerized.

Fourth, the catalyst composition may be formed by using a two-stage procedure. The first stage involves combining the molybdenum-containing compound with the organoaluminum compound in the presence of a small amount of monomer at an appropriate temperature, which is generally from about -20°C to about 80 °C. In the second stage, the foregoing reaction mixture and the hydrogen phosphite are charged in either a stepwise or simultaneous manner to the remainder of the monomer that is to be polymerized.

Fifth, an alternative two-stage procedure may also be employed. A molybdenum-ligand complex is first formed by pre-combining the molybdenum-containing compound with the hydrogen phosphite. Once formed, this molybdenum-ligand complex is then combined with the organoaluminum

compound to form the active catalyst species. The molybdenum-ligand complex can be formed separately or in the presence of the monomer that is to be polymerized. This complexation reaction can be conducted at any convenient temperature at normal pressure, but for an increased rate of reaction, it is 5 preferable to perform this reaction at room temperature or above. The temperature and time used for the formation of the molybdenum-ligand complex will depend upon several variables including the particular starting materials and the solvent employed. Once formed, the molybdenum-ligand complex can be used without isolation from the complexation reaction mixture. If desired, however, the 10 molybdenum-ligand complex may be isolated from the complexation reaction mixture before use.

When a solution of the molybdenum-based catalyst composition or one or more of the catalyst ingredients is prepared outside the polymerization system as set forth in the foregoing methods, an organic solvent or carrier is preferably 15 employed. Useful solvents include hydrocarbon solvents such as aromatic hydrocarbons, aliphatic hydrocarbons, and cycloaliphatic hydrocarbons. Non-limiting examples of aromatic hydrocarbon solvents include benzene, toluene, xylenes, ethylbenzene, diethylbenzene, mesitylene, and the like. Non-limiting examples of aliphatic hydrocarbon solvents include n-pentane, n-hexane, 20 n-heptane, n-octane, n-nonane, n-decane, isopentane, isohexanes, isopentanes, isoctanes, 2,2-dimethylbutane, petroleum ether, kerosene, petroleum spirits, and the like. Non-limiting examples of cycloaliphatic hydrocarbon solvents include cyclopentane, cyclohexane, methylcyclopentane, methylcyclohexane, and the like. Commercial mixtures of the above hydrocarbons may also be used. For 25 environmental reasons, aliphatic and cycloaliphatic solvents are highly preferred. The foregoing organic solvents may serve to dissolve the catalyst composition or ingredients, or the solvent may simply serve as a carrier in which the catalyst composition or ingredients may be suspended.

As described above, the catalyst composition of the present invention 30 exhibits very high catalytic activity for the polymerization of conjugated dienes. Some specific examples of conjugated dienes that can be polymerized include 1,3-butadiene, isoprene, 1,3-pentadiene, 1,3-hexadiene, 2,3-dimethyl-1,3-butadiene,

2-ethyl-1,3-butadiene, 2-methyl-1,3-pentadiene, 3-methyl-1,3-pentadiene, 4-methyl-1,3-pentadiene, and 2,4-hexadiene. Mixtures of two or more conjugated dienes may also be utilized in co-polymerization. The preferred conjugated dienes are 1,3-butadiene, isoprene, 1,3-pentadiene, and 1,3-hexadiene. The most 5 preferred monomer is 1,3-butadiene inasmuch as the catalyst composition of this invention advantageously has very high catalytic activity and stereoselectivity for polymerizing 1,3-butadiene into syndiotactic 1,2-polybutadiene.

The production of conjugated diene polymers, such as syndiotactic 1,2-polybutadiene, according to this invention is accomplished by polymerizing 10 conjugated diene monomers in the presence of a catalytically effective amount of the foregoing catalyst composition. There are available a variety of methods for bringing the ingredients of the catalyst composition into contact with conjugated dienes as described above. To understand what is meant by a catalytically effective amount, it should be understood that the total catalyst concentration to be 15 employed in the polymerization mass depends on the interplay of various factors such as the purity of the ingredients, the polymerization temperature, the polymerization rate and conversion desired, and many other factors. Accordingly, specific total catalyst concentration cannot be definitively set forth except to say that catalytically effective amounts of the respective catalyst ingredients should be 20 used. Generally, the amount of the molybdenum-containing compound used can be varied from about 0.01 to about 2 mmol per 100 g of conjugated diene monomers, more preferably from about 0.02 to about 1.0 mmol per 100 g of conjugated diene monomers, and even more preferably from about 0.05 to about 0.5 mmol per 100 g of conjugated diene monomers.

25 The polymerization of conjugated diene monomers according to this invention is preferably carried out in an organic solvent as the diluent. Accordingly, a solution polymerization system may be employed in which both the monomer to be polymerized and the polymer formed are soluble in the polymerization medium. Alternatively, a precipitation polymerization system may 30 be employed by choosing a solvent in which the polymer formed is insoluble. In both cases, an amount of the organic solvent in addition to the organic solvent that may be used in preparing the molybdenum-based catalyst composition is usually

added to the polymerization system. The additional organic solvent may be either the same as or different from the organic solvent contained in the catalyst solutions. It is normally desirable to select an organic solvent that is inert with respect to the catalyst composition employed to catalyze the polymerization.

5 Suitable types of organic solvents that can be utilized as the diluent include, but are not limited to, aliphatic, cycloaliphatic, and aromatic hydrocarbons. Some representative examples of suitable aliphatic solvents include n-pentane, n-hexane, n-heptane, n-octane, n-nonane, n-decane, isopentane, isohexanes, isopentanes, isoctanes, 2,2-dimethylbutane, petroleum ether, kerosene, petroleum spirits, and the like. Some representative examples of suitable cycloaliphatic solvents include cyclopentane, cyclohexane, methylcyclopentane, methylcyclohexane, and the like. Some representative examples of suitable aromatic solvents include benzene, toluene, xylenes, ethylbenzene, diethylbenzene, mesitylene, and the like. Commercial mixtures of the above hydrocarbons may also be used. For 10 environmental reasons, aliphatic and cycloaliphatic solvents are highly preferred.

15 The concentration of conjugated diene monomers to be polymerized is not limited to a special range. Generally, however, it is preferred that the concentration of the monomer present in the polymerization medium at the beginning of the polymerization be in a range of from about 3% to about 80% by weight, more preferably from about 5% to about 50% by weight, and even more 20 preferably from about 10% to about 30% by weight.

25 The polymerization of conjugated diene monomers according to this invention may also be carried out by means of bulk polymerization, which refers to a polymerization environment where no solvents are employed. Bulk polymerization can be conducted either in a condensed liquid phase or in a gas phase.

30 In performing the polymerization of conjugated diene monomers according to this invention, a molecular weight regulator may be employed to control the molecular weight of the conjugated diene polymers to be produced. As a result, the scope of the polymerization system can be expanded in such a manner that it can be used for the production of conjugated diene polymers having a wide range of molecular weights. Suitable types of molecular weight regulators that can

be utilized include, but are not limited to, α -olefins such as ethylene, propylene, 1-butene, 1-pentene, 1-hexene, 1-heptene, and 1-octene; accumulated diolefins such as allene and 1,2-butadiene; nonconjugated diolefins such as 1,6-octadiene, 5-methyl-1,4-hexadiene, 1,5-cyclooctadiene, 3,7-dimethyl-1,6-octadiene, 1,4-5 cyclohexadiene, 4-vinylcyclohexene, 1,4-pentadiene, 1,4-hexadiene, 1,5-hexadiene, 1,6-heptadiene, 1,2-divinylcyclohexane, 5-ethylidene-2-norbornene, 5-methylene-2-norbornene, 5-vinyl-2-norbornene, dicyclopentadiene, and 1,2,4-trivinylcyclohexane; acetylenes such as acetylene, methylacetylene and vinylacetylene; and mixtures thereof. The amount of the molecular weight regulator used, expressed in parts per hundred parts by weight of the conjugated diene monomers (phm), is from about 0.01 to about 10 phm, preferably from about 0.02 to about 2 phm, and more preferably from about 0.05 to about 1 phm.

10 The molecular weight of the conjugated diene polymers to be produced can also be effectively controlled by polymerizing conjugated diene monomers in 15 the presence of hydrogen gas. In this case, the preferable partial pressure of hydrogen gas is within the range of about 0.01 to about 50 atmospheres.

17 The polymerization of conjugated diene monomers according to this invention may be carried out as a batch process, a continuous process, or even a semi-continuous process. In the semi-continuous process, monomer is 20 intermittently charged as needed to replace that monomer already polymerized. In any case, the polymerization is desirably conducted under anaerobic conditions by using an inert protective gas such as nitrogen, argon or helium, with moderate to vigorous agitation. The polymerization temperature employed in the practice 25 of this invention may vary widely from a low temperature, such as -10°C or below, to a high temperature such as 100°C or above, with a preferred temperature range being from about 20°C to about 90°C. The heat of polymerization may be removed by external cooling, cooling by evaporation of the monomer or the solvent, or a combination of the two methods. Although the polymerization pressure employed may vary widely, a preferred pressure range is from about 1 atmosphere to about 30 10 atmospheres.

Once a desired conversion is achieved, the polymerization can be stopped by the addition of a polymerization terminator that inactivates the catalyst.

Typically, the terminator employed is a protic compound, which includes, but is not limited to, an alcohol, a carboxylic acid, an inorganic acid, water, or a mixture thereof. An antioxidant such as 2,6-di-*tert*-butyl-4-methylphenol may be added along with, before or after the addition of the terminator. The amount of the 5 antioxidant employed is preferably in the range of 0.2% to 1% by weight of the polymer product. When the polymerization reaction has been stopped, the polymer can be recovered from the polymerization mixture by conventional procedures of desolvantization and drying. For instance, the polymer may be isolated from the polymerization mixture by coagulation of the polymerization 10 mixture with an alcohol such as methanol, ethanol, or isopropanol, or by steam distillation of the solvent and the unreacted monomer, followed by filtration. The polymer product is then dried to remove residual amounts of solvent and water.

As noted above, a preferred embodiment of this invention is directed toward a catalyst composition for the synthesis of crystalline conjugated diene polymers such as syndiotactic 1,2-polybutadiene. Advantageously, the catalyst 15 composition of this invention can be manipulated to vary the characteristics of the resulting syndiotactic 1,2-polybutadiene. Namely, the syndiotactic 1,2-polybutadiene made utilizing the catalyst composition of the present invention can have various melting temperatures, molecular weights, 1,2-linkage contents, and 20 syndiotacticities, all of which are dependent upon the selection of the catalyst ingredients and the ingredient ratios. For example, it has been found that the melting temperature of syndiotactic 1,2-polybutadiene can be increased by synthesizing the polymer with the catalyst of this invention where the organoaluminum compound employed contains a sterically hindered hydrocarbyl 25 group. Non-limiting examples of these sterically hindered hydrocarbyl groups include isopropyl, isobutyl, *t*-butyl, and neopentyl groups, all of which have been fully disclosed above. Likewise, the use of acyclic hydrogen phosphites in lieu of cyclic hydrogen phosphites will yield syndiotactic 1,2-polybutadiene having an increased melting temperature.

30 In a preferred embodiment of this invention, syndiotactic 1,2-polybutadiene polymers having a melting temperature from about 110 °C to about 220 °C can be prepared. More preferably, syndiotactic 1,2-polybutadiene polymers

having a melting temperature from about 120 °C to about 210 °C, and even more preferably from about 130 °C to about 200 °C, can be prepared. The 1,2-linkage content is preferably from about 50 to about 99 percent, and more preferably from about 70 to about 98 percent. The syndiotacticity is preferably from about 50 to 5 about 99 percent, more preferably from about 60 to about 98 percent, and even more preferably from about 70 to about 98 percent.

The syndiotactic 1,2-polybutadiene produced with the catalyst composition of this invention has many uses. It can be blended with various rubbers in order to improve the properties thereof. For example, it can be 10 incorporated into elastomers in order to improve the green strength of those elastomers, particularly in tires. The supporting or reinforcing carcass of tires is particularly prone to distortion during tire building and curing procedures. For this reason, the incorporation of the syndiotactic 1,2-polybutadiene into rubber compositions that are utilized in the supporting carcass of tires has particular utility 15 in preventing or minimizing this distortion. In addition, the incorporation of the syndiotactic 1,2-polybutadiene into tire tread compositions can reduce the heat build-up and improve the tear and wear characteristics of tires. The syndiotactic 1,2-polybutadiene is also useful in the manufacture of films and packaging materials and in many molding applications.

20 In order to demonstrate the practice of the present invention, the following examples have been prepared and tested as described in the General Experimentation Section disclosed hereinbelow. The examples should not, however, be viewed as limiting the scope of the invention. The claims will serve to define the invention.

25

GENERAL EXPERIMENTATION

Example 1

An oven-dried 1-liter glass bottle was capped with a self-sealing rubber liner and a perforated metal cap. After the bottle was thoroughly purged with a 30 stream of dry nitrogen gas, the bottle was charged with 68 g of hexanes and 182 g of a 1,3-butadiene/hexanes blend containing 27.5% by weight of 1,3-butadiene. The following catalyst ingredients were added to the bottle in the following order:

(1) 0.15 mmol of molybdenum 2-ethylhexanoate, (2) 0.60 mmol of bis(2-ethylhexyl) hydrogen phosphite, and (3) 2.25 mmol of triisobutylaluminum. The bottle was tumbled for 6 hours in a water bath maintained at 65°C. The polymerization was terminated by addition of 10 mL of isopropanol containing 0.5 g of 2,6-di-*tert*-butyl-4-methylphenol. The polymerization mixture was coagulated with 3 liters of isopropanol. The resulting syndiotactic 1,2-polybutadiene was isolated by filtration and dried to a constant weight under vacuum at 60°C. The yield of the polymer was 47.5 g (95%). As measured by differential scanning calorimetry (DSC), the polymer had a melting temperature of 189°C. The ¹H and ¹³C nuclear magnetic resonance (NMR) analysis of the polymer indicated a 1,2-linkage content of 92.7% and a syndiotacticity of 96.0%. As determined by gel permeation chromatography (GPC), the polymer had a weight average molecular weight (M_w) of 1,209,000, a number average molecular weight (M_n) of 857,000, and a polydispersity index (M_w/M_n) of 1.5. The monomer charge, the amounts of the catalyst ingredients, and the properties of the resulting syndiotactic 1,2-polybutadiene are summarized in Table I.

Table I

Example No.	1	2	3	4	5
Hexanes (g)	68	68	68	68	68
27.5% 1,3-Bd/hexanes (g)	182	182	182	182	182
Mo 2-EHA (mmol)	0.15	0.15	0.15	0.15	0.15
HP(O)(OCH ₂ CH(Et) ₂ CH ₃) ₂ (mmol)	0.60	0.60	0.60	0.60	0.60
i-Bu ₃ Al (mmol)	2.25	1.95	2.10	2.40	2.55
Mo/P/Al molar ratio	1:4:15	1:4:13	1:4:14	1:4:16	1:4:17
Polymer yield (%) after 6 hr at 65°C	95	91	92	94	93
Melting temperature (°C)	189	189	189	189	189
M _w	1,209,000	1,273,000	1,054,000	980,000	891,000
M _n	813,000	857,000	570,000	442,000	515,000
M _w /M _n	1.5	1.5	1.9	2.2	1.7

Examples 2-5

In Examples 2-5, the procedure of Example 1 was repeated except that the catalyst ratio was varied as shown in Table I. The monomer charge, the amounts of the catalyst ingredients, and the properties of the resulting syndiotactic 5 1,2-polybutadiene produced in each example are summarized in Table 1.

Examples 6-9

In Examples 6-10, the procedure of Example 1 was repeated except that tri-n-butylaluminum was substituted for the triisobutylaluminum and the catalyst 10 ingredient ratios varied as shown in Table II. The monomer charge, the amounts of the catalyst ingredients, and the properties of the resulting syndiotactic 1,2-polybutadiene produced in each example are summarized in Table II. The ¹H and ¹³C NMR analysis of the polymer produced in Example 7 indicated a 1,2-linkage content of 87.3% and a syndiotacticity of 82.0%.

Table II

Example No.	6	7	8	9
Hexanes (g)	68	68	68	68
27.5% 1,3-Bd/hexanes (g)	182	182	182	182
Mo2-EHA (mmol)	0.15	0.15	0.15	0.15
HP(O)(OCH ₂ CH(Et)(CH ₂) ₃ CH ₃) ₂ (mmol)	0.60	0.60	0.60	0.60
n-Bu ₃ Al (mmol)	2.70	2.85	3.00	3.15
Mo/P/Al molar ratio	1:4:18	1:4:19	1:4:20	1:4:21
Polymer yield (%) after 6 hr at 65 °C	89	93	91	88
Melting temperature (°C)	142	141	142	142
M _w	510,000	474,000	487,000	445,000
M _n	301,000	274,000	255,000	243,000
M _w /M _n	1.7	1.7	1.9	1.8

Examples 10-13

In Examples 10-13, the procedure of Example 1 was repeated except that
dineopentyl hydrogen phosphite was substituted for bis(2-ethylhexyl) hydrogen
phosphite, and the catalyst ingredient ratios were varied as shown in Table III. The
5 monomer charge, the amounts of the catalyst ingredients, and the properties of the
resultant syndiotactic 1,2-polybutadiene produced in each example are summarized
in Table III.

Table III

Example No.	10	11	12	13
Hexanes (g)	68	68	68	68
27.5% 1,3-Bd/hexanes (g)	182	182	182	182
Mo2-EHA (mmol)	0.15	0.15	0.15	0.15
HP(O)(OCH ₂ CM ₃) ₂ (mmol)	0.60	0.60	0.60	0.60
<i>i</i> -Bu ₃ Al (mmol)	2.25	1.95	2.10	2.40
Mo/P/Al molar ratio	1:4:14	1:4:15	1:4:16	1:4:17
Polymer yield (%) after 6 hr at 65 °C	91	91	84	80
Melting temperature (°C)	192	192	192	192
M _w	1,204,000	1,042,000	984,000	920,000
M _n	708,000	521,000	547,000	484,000
M _w /M _n	1.7	2.0	1.8	1.9

Example 14

An oven-dried 1-liter glass bottle was capped with a self-sealing rubber liner and a perforated metal cap. After the bottle was thoroughly purged with a stream of dry nitrogen gas, the bottle was charged with 227 g of a 1,3-butadiene/hexanes blend containing 22.0 % by weight of 1,3-butadiene. The following catalyst components were added to the bottle in the following order: (1) 0.20 mmol of molybdenum 2-ethylhexanoate, (2) 0.80 mmol of bis(2-ethylhexyl)hydrogen phosphite, and (3) 10.8 mmol of isobutylaluminoxane. The bottle was tumbled for 8 hours in a water bath maintained at 65 °C. The polymerization was terminated by addition of 10 mL of isopropanol containing 1.0 g of 2,6-di-*tert*-butyl-4-methylphenol. The polymerization mixture was coagulated with 3 liters of isopropanol. The resulting syndiotactic 1,2-polybutadiene was isolated by filtration and dried to a constant weight under vacuum at 60 °C. The yield of the polymer was 43.1 g (86%). As measured by differential scanning calorimetry (DSC), the polymer had a melting temperature of 189 °C. The ¹H and ¹³C nuclear magnetic resonance (NMR) analysis of the polymer indicated a 1,2-linkage content of 92% and a syndiotacticity of 95%. As determined by gel permeation chromatography (GPC), the polymer had a weight average molecular weight (M_w) of 1,037,000, a number average molecular weight (M_n) of 432,000, and a polydispersity index (M_w/M_n) of 2.4. The monomer charge, the amounts of the catalyst ingredients, and the properties of the resulting syndiotactic 1,2-polybutadiene are summarized in Table IV.

Table IV

Example No.	14	15	16	17
22.0% 1,3-Bd/hexanes (g)	227	227	227	227
Mo2-EHA (mmol)	0.20	0.20	0.20	0.20
HP(O)(OCH ₂ CH(Et)CH ₂) ₃ CH ₃) ₂ (mmol)	0.80	0.80	0.80	0.80
Isobutylaluminoxane (mmol)	10.8	11.6	12.4	13.2
Mo/P/Al molar ratio	1:4:54	1:4:58	1:4:62	1:4:66
Polymer yield (%) after 8 hr at 65 °C	86	87	89	86
Melting temperature (°C)	189	189	189	189
M _w	1,037,000	982,000	964,000	978,000
M _n	432,000	378,000	344,000	391,000
M _w /M _n	2.4	2.6	2.8	2.5

Examples 15-17

In Examples 15-17, the procedure of Example 14 was repeated except that the catalyst ingredient ratio was varied. The monomer charge, the amounts of the catalyst ingredients, and the properties of the resulting syndiotactic 1,2-polybutadiene produced in each example are summarized in Table IV.

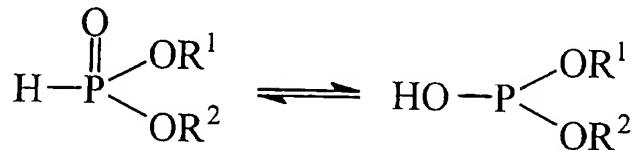
Example 18

In Example 18, the procedure of Example 1 was repeated except that the catalyst components used were 0.60 mmol of molybdenum 2-ethylhexanoate, 3.00 mmol of 2-oxo-(2H)-5-butyl-5-ethyl-1,3,2-dioxaphosphorinane and 9.00 mmol of triisobutylaluminum, and the polymerization was conducted for 12 hours at 65 °C. Work-up of the polymerization mixture in a manner similar to that described in Example 1 gave 19.1 g (38% yield) of the polymer. As measured by DSC, the polymer had a melting temperature of 167 °C. As determined by GPC, the polymer had a weight average molecular weight (M_w) of 753,000, a number average molecular weight (M_n) of 330,000, and a polydispersity index (M_w/M_n) of 2.3.

Various modifications and alterations that do not depart from the scope and spirit of this invention will become apparent to those skilled in the art. This invention is not to be duly limited to the illustrative embodiments set forth herein.

What is claimed is:

- 1 1. A catalyst composition that is the combination of or the reaction product of ingredients comprising:
 - 3 (a) a molybdenum-containing compound;
 - 4 (b) a hydrogen phosphite; and
 - 5 (c) an organoaluminum compound.
- 1 2. A catalyst composition formed by a process comprising the step of combining:
 - 2 (a) a molybdenum-containing compound;
 - 3 (b) a hydrogen phosphite; and
 - 4 (c) an organoaluminum compound.
- 1 3. A process for preparing conjugated diene polymers comprising the step of:
 - 2 polymerizing conjugated diene monomers in the presence of a catalytically effective amount of a catalyst composition formed by combining:
 - 4 (a) a molybdenum-containing compound;
 - 5 (b) a hydrogen phosphite; and
 - (c) an organoaluminum compound.
- 1 4. The catalyst composition of claim 1 or 2, or the process of claim 3, where the hydrogen phosphite is an acyclic hydrogen phosphite defined by the following keto-enol tautomeric structures:



10 or a cyclic hydrogen phosphite defined by the following keto-enol tautomeric
11 structures:

12

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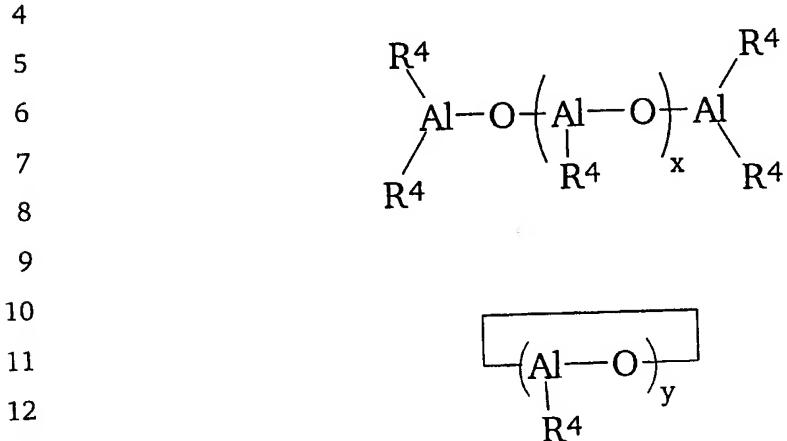
19 or a mixture thereof, where R^1 and R^2 , which may be the same or different, are
20 mono-valent organic groups, and where R^3 is a divalent organic group.

1 5. The catalyst composition of claim 4, where R^1 and R^2 are alkyl, cycloalkyl,
2 substituted cycloalkyl, alkenyl, cycloalkenyl, substituted cycloalkenyl, aryl, allyl,
3 substituted aryl, aralkyl, alkaryl, or alkynyl groups, with each group containing up
4 to about 20 carbon atoms, and where R^3 is an alkylene, cycloalkylene, substituted
5 alkylene, substituted cycloalkylene, alkenylene, cycloalkenylene, substituted
6 alkenylene, substituted cycloalkenylene, arylene, or substituted arylene group, with
7 each group containing up to about 20 carbon atoms.

1 6. The catalyst composition of claim 1 or 2, or the process of claim 3, where the
2 organoaluminum compound is defined by the formula AlR_nX_{3-n} , where each R ,
3 which may be the same or different, is a mono-valent organic group, where each
4 X , which may be the same or different, is a hydrogen atom, a halogen atom, a
5 carboxylate group, an alkoxide group, or an aryloxide group, and where n is an
6 integer including 1, 2 or 3.

1 7. The catalyst composition of claim 6, where each R is an alkyl, cycloalkyl,
2 substituted cycloalkyl, alkenyl, cycloalkenyl, substituted cycloalkenyl, aryl, allyl,
3 substituted aryl, aralkyl, alkaryl, or alkynyl group, with each group containing up
4 to about 20 carbon atoms, and where each X is a halogen atom, a carboxylate
5 group, an alkoxide group, or an aryloxide group, with each group containing up to
6 about 20 carbon atoms.

1 8. The catalyst composition of claim 1 or 2, or the process of claim 3, where the
2 organoaluminum compound comprises an aluminoxane defined by one of the
3 following formulas:



14
15 where x is an integer of 1 to about 100, y is an integer of 2 to about 100, and each
16 R⁴, which may be the same or different, is a mono-valent organic group.

1 9. The catalyst composition of claim 8, where each R⁴ is an alkyl, cycloalkyl,
2 substituted cycloalkyl, alkenyl, cycloalkenyl, substituted cycloalkenyl, aryl, allyl,
3 substituted aryl, aralkyl, alkaryl, or alkynyl group, with each group containing up
4 to about 20 carbon atoms.

1 10. A syndiotactic 1,2-polybutadiene polymer that has been prepared by
2 polymerizing 1,3-butadiene monomer by using the composition of claims 1 or 2 as
3 a catalyst.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 00/10274

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C08F136/06 C08F4/69

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	DE 14 20 558 A (MONTECATINI) 24 October 1968 (1968-10-24) example 6 ---	1-3, 6, 7, 10
A	EP 0 222 189 A (BUNAWERKE HUELS GMBH) 20 May 1987 (1987-05-20) claims -----	1-3, 6, 7, 10

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

* Special categories of cited documents :

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- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

T later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

X document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

Y document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

& document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
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INTERNATIONAL SEARCH REPORT

Int'l Application No
PCT/US 00/10274

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